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<b>(54) Title:</b> COSMETIC COMPOSITIONS			
<b>(57) Abstract</b> Cosmetic composition in the form of a multiphase oil-in-water emulsion wherein the composition comprises at least two internal oil phases, a first oil phase having water dispersed therein and a second oil phase which is water free, and wherein the average size of disperse phase particles in the first oil phase is at least about 10 microns and the average size of disperse phase particles in the second oil phase is less than about 5 microns. The compositions of the invention exhibit improved product stability, moisturisation, skin feel and appearance and shine/oil control.			

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Cosmetic CompositionsTechnical Field

The present invention relates to cosmetic compositions. In particular it relates to cosmetic compositions in the form of emulsions which provide improved product stability, moisturisation, skin feel and appearance and shine/oil control.

Background of the Invention

Skin is made up of several layers of cells which coat and protect the keratin and collagen fibrous proteins that form the skeleton of its structure. The outermost of these layers, referred to as the stratum corneum, is known to be composed of 25nm protein bundles surrounded by 8nm thick layers. Anionic surfactants and organic solvents typically penetrate the stratum corneum membrane and, by delipidization (i.e. removal of the lipids from the stratum corneum), destroy its integrity. This destruction of the skin surface topography leads to a rough feel and may eventually permit the surfactant or solvent to interact with the keratin, creating irritation.

It is now recognised that maintaining the proper water gradient across the stratum corneum is important to its functionality. Most of this water, which is sometimes considered to be the stratum corneum's plasticizer, comes from inside the body. If the humidity is too low, such as in a cold climate, insufficient water remains in the outer layers of the stratum corneum to properly plasticize the tissue, and the skin begins to scale and becomes itchy. Skin permeability is also decreased somewhat when there is inadequate water across the stratum corneum. On the other hand, too much water on the outside of the skin causes the stratum corneum to ultimately sorb three to five times its own weight of bound water. This swells and puckers the skin and results in approximately a two to three fold increase in the permeability of the skin to water and other polar molecules.

Thus, a need exists for compositions which will assist the stratum corneum in maintaining its barrier and water-retention functions at optimum performance in spite of deleterious interactions which the skin may encounter in washing, work, and recreation.

Conventional cosmetic cream and lotion compositions as described, for example, in Sagarin, Cosmetics Science and Technology, 2nd Edition, Vol. I, Wiley Interscience (1972) and Encyclopaedia of Chemical Technology, Third Edition, Volume 7 are known to provide varying degrees of emolliency, barrier and water-retention (moisturizing) benefits. However, they can also suffer serious negatives in terms of skin feel (i.e. they often feel very greasy on the skin) as well as having poor rub-in, absorption and residue characteristics.

The present invention therefore provides skin-care cosmetic compositions which provide improvements in product stability, moisturisation, skin feel and appearance and shine/oil control.

#### Summary of the Invention

According to one aspect of the present invention a cosmetic composition in the form of an emulsion having an internal aqueous phase and which comprises:

- (a) from about 0.1% to about 20% by weight of a water-soluble calcium salt of an organic or inorganic acid; and
- (b) from about 0.01% to about 10% by weight of non-volatile, silicone surfactant.

According to a second aspect of the present invention there is provided cosmetic composition in the form of a multiphase oil-in-water emulsion wherein the composition comprises at least two internal oil phases, a first oil phase having water dispersed therein and a second oil phase which is water free, and wherein the average size of disperse phase particles in the first oil phase is at least about 10 microns and the average size of disperse phase particles in the second oil phase is less than about 5 microns.

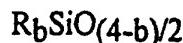
The compositions of the invention provide improved product stability, skin feel and appearance, application and skin absorption characteristics and shine/oil control.

All levels and ratios are by weight of total composition, unless otherwise indicated. Chain length and degree of ethoxylation are also specified on a weight average basis.

Detailed Description of the Invention

According to the first aspect of the present invention a first essential component of the composition herein is a water-soluble calcium salt of an organic or inorganic acid. The term "water-soluble" herein means that the salt has a solubility of at least about 1% in water at 25°C. Suitable calcium salts for use herein include calcium chloride, calcium pantothenate, calcium acetate, calcium acetyl salicylate, calcium ascorbate, calcium chloride, calcium cyclamate, calcium gluconate, calcium lactate and calcium nitrate, and mixtures thereof, preferably calcium pantothenate. The calcium salt is present at a level of from about 0.1% to about 20%, preferably from about 1.0% to about 15% by weight.

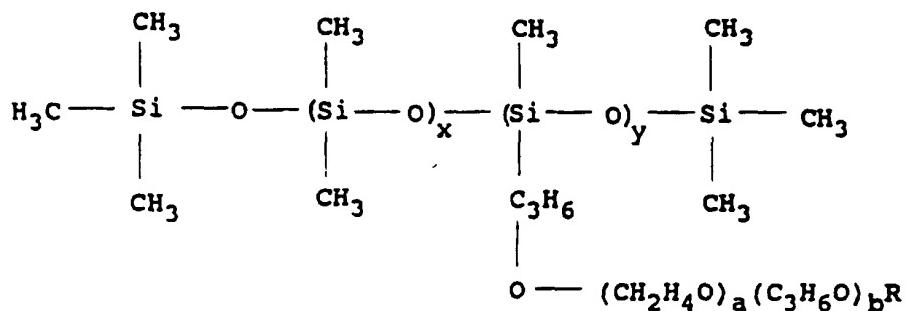
A second essential component of the composition according to the first aspect of the present invention is a non-volatile silicone surfactant. The non-volatile silicone surfactant is preferably selected from polyorganosiloxanes-polyoxyalkylene copolymers containing at least one polydiorganosiloxane segment and at least one polyoxyalkylene segment, said polydiorganosiloxane segment consisting essentially of



siloxane units wherein b has a value of from about 0 to about 3, inclusive, there being an average value of approximately 2 R radicals per silicon for all siloxane units in the copolymer, and R denotes a radical selected from methyl, ethyl, vinyl, phenyl and a divalent radical bonding said polyoxyalkylene segment to the polydiorganosiloxane segment, at least about 95% of all R radicals being methyl; and said polyoxyalkylene segment having an average molecular weight of at least about 1000 and consisting of from about 0 to about 50 mol percent polyoxypropylene units and from about 50 to about 100 mol percent polyoxyethylene units, at least one terminal portion of said polyoxyalkylene segment being bonded to said polydiorganosiloxane segment, any terminal portion of said polyoxyalkylene segment not bonded to said polydiorganosiloxane segment being satisfied by a terminating radical; the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in said

copolymer having a value of from about 2 to about 8. Such polymers are described in US-A-4,268,499.

Suitable non-volatile silicone surfactants for use herein are selected from polydiorganosiloxane- polyoxyalkylene copolymers having the formula (I):

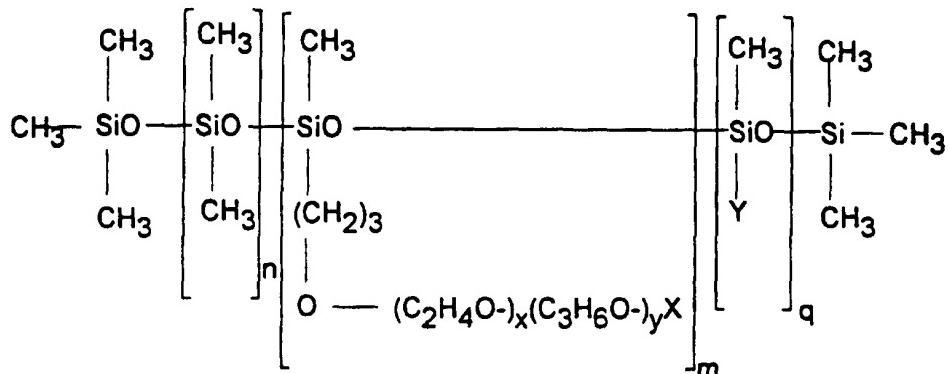


wherein x and y are selected such that the weight ratio of polydiorganosiloxane segments to polyoxalkylene segments is from about 2 to about 8, the mol ratio of a:(a+b) is from about 0.5 to about 1, and R is a chain terminating group, especially selected from hydrogen; hydroxyl; alkyl, such as methyl, ethyl, propyl, butyl, benzyl; aryl, such as phenyl; alkoxy such as methoxy, ethoxy, propoxy, butoxy; benzyloxy; aryloxy, such as phenoxy; alkynyoxy, such as vinyloxy and allyloxy; acyloxy, such as acetoxy, acryloxy and propionoxy and amino, such as dimethylamino.

The number of and average molecular weights of the segments in the copolymer are such that the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in the copolymer is preferably from about 2.5 to about 4.0.

Suitable copolymers of the type described hereinabove are available commercially under the tradenames Belsil (RTM) from Wacker-Chemie GmbH, Geschäftsbereich S, Postfach D-8000 Munich 22 and Abil (RTM) from Th. Goldschmidt Ltd., Tego House, Victoria Road, Ruislip, Middlesex, HA4 0YL. Particularly preferred for use herein are Belsil (RTM) 6031 and Abil (RTM) B88183.

Other suitable non-volatile silicone surfactants can be selected from alkyl- or alkoxy-methicone or dimethicone copolyols having the formula (II):



(II)

where X is a hydrogen atom, an alkyl, an alkoxy or an acyl group having from 1 to 16 carbon atoms, Y is C<sub>8</sub>-C<sub>22</sub> alkoxy or alkyl radical, n = 0 to 200, m = 1 to 40 and q = 1 to 100, the molecular weight of the residue (C<sub>2</sub>H<sub>4</sub>O-)<sub>x</sub>(C<sub>3</sub>H<sub>6</sub>O-)<sub>y</sub>X being from 250 to 2000, x and y being selected so that the weight ratio of the oxyethylene/oxypropylene groups is between about 100 : 0 and 20 : 80.

Especially preferred herein from the viewpoint of product stability is laurylmethicone copolyol.

The non-volatile silicone surfactant is present herein at a level of from 0.01% to about 10%, preferably from about 0.01% to about 5%, by weight.

Preferably the cosmetic compositions herein additionally comprise volatile silicone oil. Suitable volatile silicone oils for use herein include cyclic polyorganosiloxanes having viscosities of less than about 10 centistokes and linear polyorganosiloxanes having viscosities of less than about 5 centistokes at 25°C, and mixtures thereof. Preferably the volatile silicone oil is selected from cyclic polydimethylsiloxanes containing from about 3 to about 9 silicon atoms, preferably containing from about 4 to about 6

silicon atoms and linear polydimethylsiloxanes containing from about 3 to about 9 silicon atoms. Most preferred for use herein is dimethicone fluid.

The volatile silicone oil is present at a level of from about 0.1% to about 20%, preferably from about 0.1% to about 10% by weight.

The cosmetic composition of the invention takes the form of an emulsion having an internal aqueous phase, for example a water-in-oil emulsion containing from about 10% to about 40%, preferably from about 15% to about 30%, especially from about 15% to about 25% by weight of oil. From the viewpoint of product stability and shine/oil control however, the cosmetic composition is preferably formulated as a multiphase emulsion having both an internal aqueous phase and multiple internal oil phases. Hence according to a second aspect of the present invention there is provided a cosmetic composition in the form of a multiphase oil-in-water emulsion wherein the composition comprises at least two internal oil phases, a first oil phase having water dispersed therein (hereinafter the water-in-oil phase) and a second oil phase which is water free (hereinafter the oil phase), and wherein the average size of disperse phase particles in the first oil phase is at least about 10 microns, preferably between about 10 microns and about 50 microns, and the average size of disperse phase particles in the second oil phase is less than about 5 microns. The aqueous continuous phase of the multiphase emulsion preferably comprises a liquid crystalline or gel network.

The compositions of the second aspect of the present invention preferably comprise a nonionic surfactant or mixture of nonionic surfactants having an average HLB of from about 7 to about 12. Suitable nonionic surfactants for use herein can be selected from polyethylene glycol ethers of C<sub>8</sub>-C<sub>22</sub>-fatty alcohols, preferably steareth-2 and steareth-21, and mixtures thereof. The nonionic surfactant must be capable of forming a gel network in the aqueous continuous phase. A preferred nonionic surfactant for use herein is commercially available under the tradename Brij 72/721.

The nonionic surfactant is present in the compositions herein at a level of from about 0.1% to about 20%, preferably from about 0.1% to about 10% by weight.

In the compositions according to the second aspect of the present invention the water-in-oil phase preferably comprises from about 10% to about 90%, preferably from about 10% to about 75%, by weight thereof of water, from about 0.1% to about 20% by weight thereof of a water-soluble calcium salt of an organic or inorganic acid, and from about 0.01% to about 10% by weight thereof of non-volatile, silicone surfactant, these levels being by weight of the water-in-oil phase.

The compositions herein preferably further comprise from about 5 to about 30%, preferably from about 5% to about 20% by weight of volatile or non-volatile hydrocarbon oil. Suitable hydrocarbon oils for use herein include mineral oil, microcrystalline wax petrolatum, isododecane, isoheptadecane, isoeicosane, isodecane, decane, hexadecane, dodecane, tetradecane and octadecane, and mixtures thereof.

#### Preparation of Multiphase Emulsion Compositions

The multiphase emulsion compositions can be prepared as follows. A first water-in-oil emulsion is prepared under high shear using standard emulsification techniques. A second oil-in-water emulsion is also separately prepared under high shear. The two emulsions are then mixed carefully by avoiding excessive shear and heat to form a multiphase emulsion having both an internal aqueous phase and multiple internal oil phases. The level of water-in-oil emulsion present in the mixture is from about 1% to about 40%, preferably from about 5% to about 25% by weight of the mixture. The mixing ratio of water-in-oil emulsion to oil-in-water emulsion is in the range from about 99:1 to about 1:99, preferably from about 1:1 to about 1:20.

The Examples below illustrate water-in-oil and multiphase emulsions of the invention.

#### Examples

##### 1. Water-in-oil emulsions

	I/%	II/%	III/%	IV/%	V/%
Laurylmethicone Copolyol	2.0	2.5	2.3	2.1	2.0
PPG-3 Myristyl Ether	0.5	0.7	0.55	0.45	0.5
Cyclomethicone	4.0	4.5	5.0	3.9	0.0
Isohexadecane	15.0	20.0	18.0	15.5	19.0
Dimethicone	3.0	4.5	3.5	3.2	3.1
Octyl Stearate	0.0	5.0	1.0	0.5	5.5
Calcium Panthenate	10.0	11.5	10.5	10.0	10.0
FD&C Red No.4 C.I. 14700 & water	1.0	1.5	1.0	1.0	1.0
Water				----- to 100 -----	

2. Multiphase oil-in-water emulsion comprising two internal oil phases

	VI/%	VII/%	VIII/%	IX/%	X/%
	to 100				
Water					
Butylene Glycol	8.0	8.0	10.0	9.5	8.5
Xanthan Gum	0.2	0.1	0.15	0.25	0.1
Hectorite	0.25	0.3	0.29	0.28	0.3
Glycerin	5.0	6.0	5.2	4.5	5.0
Steareth-2	2.2	2.1	2.0	1.9	2.3
Steareth-21	1.0	1.2	1.5	1.0	1.3
Isocetyl Stearate	3.0	3.0	3.0	3.0	3.0
Tocopheryl Acetate	2.1	2.0	2.3	2.2	2.0
Cetearyl Alcohol	1.6	1.7	1.5	1.5	1.55
Octyl Methoxycinnamate	4.0	4.5	4.2	4.1	4.3
Propylene Glycol Stearate	1.2	1.0	1.0	1.1	1.5
Glyceryl Stearate	1.1	1.0	1.0	1.1	1.2
Dimethicone	2.0	2.1	2.5	3.0	2.0
Cetyl Palmitate	1.0	1.0	1.0	1.5	1.0
SD Alcohol 39C	6.0	5.5	5.5	6.0	6.0
W/O Emulsion	20.0	21	25	15	20
(from any of Examples I-V)					
Shea Butter	0.0	1.2	1.5	2.0	1.8
Babassu Oil	0.0	0.5	1.0	0.9	2.0
Cetearyl Isononanoate	3.0	4.0	2.0	6.0	3.0

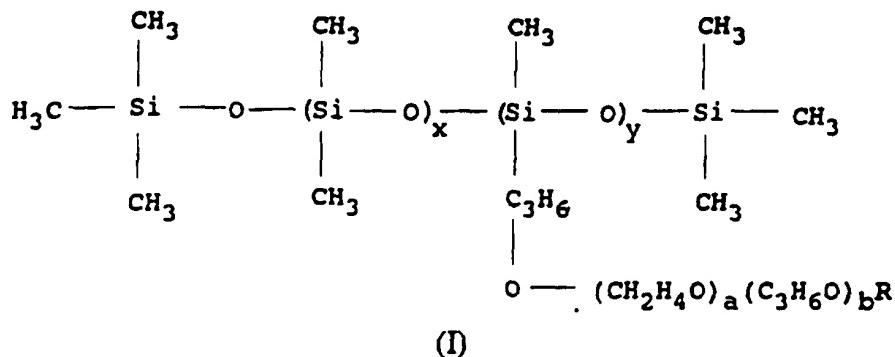
The multiphase emulsion compositions of the invention exhibit improved product stability, aesthetics and cosmetic properties. The multiphase emulsion compositions are also valuable from the viewpoint of keeping incompatible components apart, e.g. calcium in the internal water phase is kept apart from the alcohol and glycol materials with which the calcium is incompatible in the above examples VI-X.

CLAIMS:

1. A cosmetic composition in the form of a multiphase oil-in-water emulsion wherein the composition comprises at least two internal oil phases, a first oil phase having water dispersed therein and a second oil phase which is water free, and wherein the average size of disperse phase particles in the first oil phase is at least about 10 microns and the average size of disperse phase particles in the second oil phase is less than about 5 microns.
2. A cosmetic composition according to Claim 1 wherein the aqueous continuous phase comprises a liquid crystalline or gel network.
3. A cosmetic composition according to Claim 1 or 2 comprising nonionic surfactant or mixture of nonionic surfactants having an average HLB of from about 7 to about 12.
4. A cosmetic composition according to Claim 3 wherein the nonionic surfactant is selected from polyethylene glycol ethers of C<sub>8</sub>-C<sub>22</sub> fatty alcohols.
5. A cosmetic composition according to Claim 4 wherein the polyethylene glycol ether of a C<sub>8</sub>-C<sub>22</sub> fatty alcohol is selected from steareth-2 and steareth-21, and mixtures thereof.
6. A cosmetic composition according to any of Claims 1 to 5 wherein the first water-containing oil phase comprises (by weight thereof):
  - (a) from about 10% to about 90% by weight of water;
  - (a) from about 0.1% to about 20% by weight of a water-soluble calcium salt of an organic or inorganic acid; and
  - (b) from about 0.01% to about 10% by weight of non-volatile, silicone surfactant.
7. A cosmetic composition according to Claim 6 wherein the non-volatile silicone surfactant is selected from polyorganosiloxanes-polyoxyalkylene copolymers containing at least one

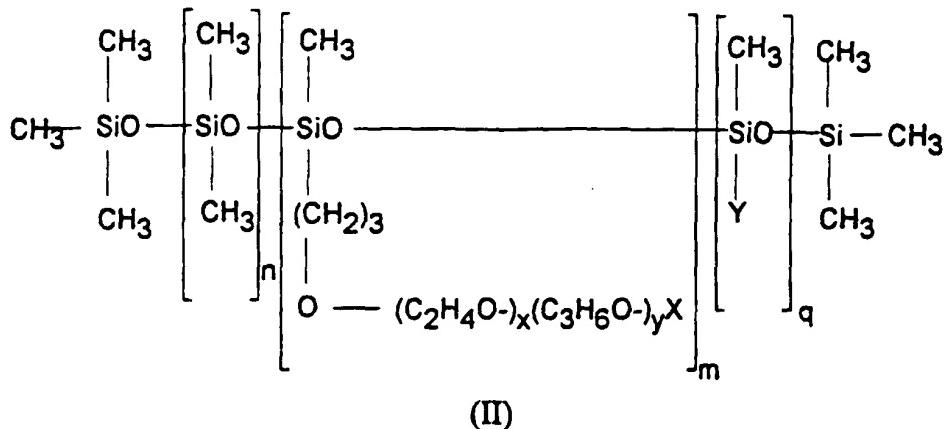
polyorganosiloxane or polydiorganosiloxane segment and at least one polyoxyalkylene segment.

8. A cosmetic composition according to Claim 7 wherein the non-volatile silicone surfactant is selected from polydiorganosiloxane-polyoxyalkylene copolymers having the formula (I):



wherein x and y are selected such that the weight ratio of polydiorganosiloxane segments to polyoxalkylene segments is from about 2 to about 8, the mol ratio of a:(a+b) is from about 0.5 to about 1, and R is a chain terminating group, especially selected from hydrogen; hydroxyl; alkyl, such as methyl, ethyl, propyl, butyl, benzyl; aryl, such as phenyl; alkoxy such as methoxy, ethoxy, propoxy, butoxy; benzyloxy; aryloxy, such as phenoxy; alkynyoxy, such as vinyloxy and allyloxy; acyloxy, such as acetoxy, acryloxy and propionoxy and amino, such as dimethylamino.

9. A cosmetic composition according to Claim 7 wherein the non-volatile silicone surfactant is selected from an alkyl- or alkoxy-methicone or dimethicone copolyol having the formula (II):



where X is a hydrogen atom, an alkyl, an alkoxy or an acyl group having from 1 to 16 carbon atoms, Y is C<sub>8</sub>-C<sub>22</sub> alkoxy or alkyl radical, n = 0 to 200, m = 1 to 40 and q = 1 to 100, the molecular weight of the residue (C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>(C<sub>3</sub>H<sub>6</sub>O)<sub>y</sub>X being from 250 to 2000, x and y being selected so that the weight ratio of the oxyethylene/oxypropylene groups is between about 100 : 0 and 20 : 80.

10. A cosmetic composition according to Claim 9 wherein the non-volatile silicone surfactant is laurylmethicone copolyol.
11. A cosmetic composition according to any of Claims 1 to 10 comprising 0.1% to about 10% by weight of volatile silicone oil.
12. A cosmetic composition according to Claim 11 wherein the volatile silicone oil is selected from cyclic polyorganosiloxanes having viscosities of less than about 10 centistokes and linear polyorganosiloxanes having viscosities of less than about 5 centistokes at 25°C, and mixtures thereof.
13. A cosmetic composition according to Claim 12 wherein the volatile silicone oil is selected from cyclic polydimethylsiloxanes containing from about 3 to about 9 silicon atoms, preferably containing from about 4 to about 5 silicon atoms and linear polydimethylsiloxanes containing from about 3 to about 9 silicon atoms.

14. A cosmetic composition according to any of Claims 1 to 12 comprising from about 1% to about 30%, preferably from about 5% to about 20% by weight volatile or non-volatile of hydrocarbon oil selected from mineral oil, microcrystalline wax petrolatum, isododecane, isohexadecane, isoeicosane, isodecane, decane, hexadecane, dodecane, tetradecane and octadecane, and mixtures thereof.
15. Process for preparing a cosmetic composition according to any of Claims 1 to 13 comprising the steps of:
  - (a) preparing a water-in-oil emulsion;
  - (b) preparing an oil-in-water emulsion;
  - (c) mixing the water-in-oil emulsion and the oil-in-water emulsion in a weight ratio of from about 99:1 to about 1:99, preferably from about 1:1 to about 1:20.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/12776

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : A61K 31/74

US CL : 424/78.03

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/78.03

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,268,499 (KEIL) 19 May 1981, see the entire document.	1-5

 Further documents are listed in the continuation of Box C.  See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

07 FEBRUARY 1996

Date of mailing of the international search report

29.02.96

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/12776

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 6-15  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.